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Enhanced Performance of Flexible Dye-Sensitized Solar Cell based on Nickel Sulfide/Polyaniline/Titanium Counter Electrode

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ABSTRACT

A novel titanium foil substrate strategy for the synthesis of high electrocatalytic activity nickel sulfide/polyaniline/titanium (NiS/PANI/Ti) composite film with one-dimensional (1D) net-work structure by using an in situ electropolymerization route, and proposed as platinum (Pt)-free counter electrode (CE) catalyst for flexible dye-sensitized solar cells (FDSSCs). The photovoltaic performance of the FDSSC based on the NiS/PANI/Ti CE exhibits *Jsc* of 14.56 mA · cm^{-2},*Voc* of 0.743 V, *FF* of 0.68, and corresponding to the η of 7.35%, much higher photoelectric conversion efficiency than that of Pt/Ti CE (6.24%). The NiS/PANI/Ti CE with 1D net-work structure is characterized by using the scanning electron microscopy (SEM), energy dispersive spectrometer (EDS), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and Tafel polarization plots. The NiS/PANI/Ti CE presents multiple functions, i.e., excellent conductivity, great electrocatalytic ability for iodine/triiodine, and lower charge transfer resistance of $1.48 \pm 0.02\ \Omega \cdot cm^2$ compared to the Pt/Ti electrode ($2.25 \pm 0.02\ \Omega \cdot cm^2$). The photocurrent-photovoltage (*J-V*) character curves are further used to calculate theoretical short-current densities and open-circuit voltage of the devices. Therefore, the NiS/PANI/Ti CE with 1D net-work structure can be considered as a promising and efficient CE for FDSSCs.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been considered as the much potential next-generation photovoltaic devices for they are herein developed and exhibited advantages, e.g., feasible, low cost, environment-friendly, high efficiency and so on [1–3]. Besides, the flexible DSSC (FDSSC) has attracted a great deal of research interests [4] due to its shape or surface can be devised and constructed as needed, the technique of large-scale roll-to-roll processing and rapid coating, which could be a promising solution for many impending energy and environmental issues.

The counter electrode (CE), as the most important component in a FDSSC, collects the electrons from the external circuit and catalyzes the reduction of triiodine (I_3^-) to iodine (I^-) between the CE and electrolyte interface. Thus, the ideal materials of CE for FDSSCs should be with high electrical conductivity for the electrons transporting and collecting, large specific surface area for the CE/electrolyte contact, and high catalytic activity for the reaction of $I_3^-$to I^-. In this respect, nickel sulfide (NiS) with high catalytic activity is an excellent catalyst for the redox couples I^-/I_3^-in FDSSCs [5,6]. For instance, Sun et al. [7] reported that NiS CE electrodeposited using a potential reversal technique and showed high catalytic activity for the reduction of $I_3^-$to I^-. Ku et al. [8] prepared a highly transparent NiS CE by using an electrodeposition technique and presented a good photovoltaic performance for thiolate/disulfide mediated DSSCs. Therefore, NiS is a good candidate for an efficient CE in electronics, optoelectronics, and memory devices. Simultaneously, the polyaniline (PANI) with one-dimensional (1D) nanofibers also is one of the most promising conducting polymers as an efficient CE in optoelectronic devices for its low cost, simple fabrication process, high electrochemical activity and environmental stability [9–12]. In addition, it is well known that Ti foils have been utilized to manufacture FDSSCs as anode and counter electrode materials for its flexibility, low sheet resistance, superior corrosion resistances in the contacting I^-/I_3^-electrolyte [13,14]. According to our previous report, the electrocatalytic activity and conductivity of CE for DSSCs can be further enhanced for the synergistic catalytic effect of two kinds or more materials with conductive and catalytic properties.

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So, in our present study, it is envisaged that a counter electrode of PANI/Ti is decorated with NiS by using two-step cyclic voltammetry approach, and served as Pt-free CE for the first time in FDSSCs. The NiS/PANI/Ti CE shows excellent electrocatalytic activity and low charge transfer resistance of $1.48 \pm 0.02\ \Omega \cdot cm^2$, which are demonstrated by the results of cyclic voltammetry (CV), electrochemical impendence spectroscopy (EIS) and Tafel curves measurements. The FDSSC fabricated with the NiS/PANI/Ti CE exhibits a greatly improved in power conversion performance of 7.35% under irradiation of 100 $mW \cdot cm^{-2}$ (AM 1.5).

2. Experimental

2.1. Materials

The nickel (II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, 98%), thiourea (TU, ≥ 99.0%), acetone, acetonitrile, ethanol, polyethylene glycol with average molecular weight of 20,000 (PEG 20,000), 4-tert-butyl-pyridine (TBP), aniline, sulfuric acid (H_2SO_4), potassium persulfate ($K_2S_2O_8$), perchloric acid ($HClO_4$), hydrochloric acid (HCl), flexible Ti foils (0.25 mm thickness) and titanium tetrachloride ($TiCl_4$) were purchased from Shanghai Chemical Agent Ltd China. All reagents are of analytical reagent grade.

Conductive flexible plate (flexible ITO/PEN, sheet resistance 6 $\Omega \cdot cm^{-2}$, thickness 0.175 ± 0.05 mm, purchased from Shenzhen Huanan Xiangcheng Technology Co., Ltd. China) was used as substrate for precipitating TiO_2 porous film and was cut into $1 \times 2\ cm^2$ sheets carefully and ultrasonically cleaned sequentially in detergent, acetone, distilled water and ethanol for 30 min, respectively; and then stored in isopropyl alcohol; the organometallic compound sensitized dye Z-907 *cis*-bis (isothiocyanato) (2, 2'-bipyridyl-4,4'-dicarboxylato) (2,2′-bipyridyl-4,4′-di-nonyl) ruthenium (II) was obtained from Solaronix SA (Switzerland). Flexible Ti foils was used as the substrate for the preparation of high electrocatalytic activity NiS/PANI/Ti due to its excellent electrical conductivity, plasticity and resisted corrosion of I^-/I_3^-electrolyte. Ti foils were cut into $1 \times 2\ cm^2$ carefully and ultrasonically cleaned sequentially in detergent, acetone and distilled water for 30 min, respectively; then immersed in 0.20 mM hydrofluoric acid solution for 10 min and rinsed in distilled water again; and then stored in ethanol.

2.2. Preparation of the NiS/PANI/Ti CE

A two-step cyclic voltammetry approach synthesized NiS/PANI/Ti CE. Firstly, the electrodeposition of PANI onto Ti substrate was carried out with an electrochemical analyzer system (CHI660B, Shanghai Chenhua Device Company, China). All experiments were implemented in a three-electrode cell at room temperature (about 25 °C), including one Pt foil as counter electrode, one Ag/AgCl electrode as reference electrode and Ti substrate with an exposed area of $0.8 \times 1\ cm^2$ as the working electrode. The base polymerization solution consisted of 0.5 M aniline and 1.0 M $HClO_4$ solution. A constant potential of −1.2 V vs. Ag/AgCl was employed for the electrodeposition of PANI on a Ti substrate. The obtained PANI/Ti CE was put into anhydrous ethanol for 0.5 h and vacuum oven at 80 °C for 12 h. Secondly, the NiS/PANI/Ti CE preparation outlined below. The obtained PANI/Ti CE as the working electrode soaked 0.05 M $NiCl_2$ and 1.0 M TU solution to carry out the electrodeposition procedure. The Ti foil substrate coated with NiS/PANI film was put into anhydrous ethanol for 0.5 h and vacuum oven at 80 °C for 12 h, respectively. Then, the NiS/PANI/Ti counter electrode with thickness of 520 nm is obtained. The electrochemical deposition parameters (EDPs) for NiS/PANI/Ti CEs prepared by the electrodeposition are listed in Table 1. For comparison, the Pt/Ti electrode and NiS/Ti electrode were prepared using a similar three-electrode system. The Ti substrates were soaked 0.01 M H_2PtCl_6 ethanol solution contained of suitable $LiClO_4$ and 0.05 M $NiCl_2$ and 1.0 M TU solution to carry out the electrodeposition procedure.

2.3. Fabrication of FDSSC

A TiO_2 anode is prepared as described previously [15–17]. Briefly, a certain amount of treated P25, absolute ethanol and distilled water were mixed with mole ratio of 1:5:1 and turned to an autoclave (packing volume < 80%) followed by a hydrothermally treatment at 200 °C for 24 h under a stirring condition, then cooling in room temperature, thus a homogeneous and stable TiO_2 colloid was obtained. The TiO_2 with particle size of 10–20 nm was coated on ITO/PEN substrate by using doctor-scraping technique. The TiO_2/ITO/PEN film was irradiated under UV light for 30 min, and then heated in vacuum oven at 80 °C for 1 h. The process was repeated for two times. The obtained TiO_2/ITO/PEN flexible film was immersed in 0.3 mM of dye Z907 Tert-butanol/acetonitrile solution for 12 h. Thus the dye-sensitized TiO_2/ITO/PEN anode with thickness of 6–8 μm was obtained. The FDSSC was fabricated by injecting the liquid electrolyte (0.05 M of I_2, 0.1 M of LiI, 0.6 M of tetrabutylammonium iodide and 0.5 M of TBP in acetonitrile) in the aperture between the dye-sensitized TiO_2/ITO/PEN electrode and above mentioned CEs. The two electrodes were clipped together and wrapped with thermoplastic hot-melt Surlyn.

2.4. Characterization

The surface morphology of the sample was observed by using JSM-7001F field emission scanning electron microscope (SEM). Energy dispersive spectroscopy analysis (EDS) was obtained from Bruker-ASX (Model Quan-Tax 200). Cyclic voltammetry (CV), electrochemical impendence spectroscopy (EIS) were conducted by using a computer-controlled electrochemical analyzer (CHI 660B, CH Instrument). The electrolyte used in the FDSSC test was also injected into the symmetric dummy cells for both EIS measurements. EIS was carried out using a CHI660B (Shanghai Chenhua Device Company, China) electrochemical measurement system at a constant temperature of 25 °C in ambient atmosphere under dark conditions and leaving an exposed area of 0.8 cm^2. The frequency of applied sinusoidal AC voltage signal was varied from 0.1 Hz to 10^5 Hz and the corresponding amplitude was kept at 5 mV in all cases.

The photovoltaic test of FDSSC with an exposed area of $0.4 \times 0.7\ cm^2$ was implemented by measuring photocurrent-photovoltage (*J-V*) character curve under white light irradiation of 100 $mW \cdot cm^{-2}$ (AM 1.5 G) came from the solar simulator (XQ-500 W, Shanghai Photoelectricity Device Company, China) in

Table 1
Electrochemical deposition parameters (EDPs) for the various counter electrodes.

EDPs / CEs	Init/V	High E/V	Low E/V	Scan Rate/V/s	Segment	Smpl Interval/V	Quiet Times/s	Sensitivity/A/V
PANI	0.4	0.4	-1.2	0.01	10	0.001	2	0.001
NiS	0.4	0.4	-1.2	0.03	8	0.001	2	0.001